

Application of Capillary Electrophoresis to Anion Speciation in Soil Water Extracts:

II. Arsenic

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ABSTRACT

A method has been developed for the speciation of arsenic (AsO_2^- , AsO_4^{3-} , and dimethylarsinic [DMA]) in natural soil solutions from contaminated sites in Australia. The separation of these anions was achieved by capillary zone electrophoresis (CZE) using a fused silica capillary (72-cm by 50- μm i.d.) with a basic chromate buffer and on-column indirect UV detection at 254 nm. Method parameters, such as electrolyte pH, run voltage, and capillary temperature were studied in order to establish suitable analytical conditions. The ideal separation for As(III) and DMA was achieved with a buffer pH of 8.0, a run voltage of 25 kV, and a capillary temperature of 30°C. Under these conditions, As(V) and orthophosphate ions comigrated. However, the use of a chromate buffer at pH 10, a run voltage of 20 kV, and capillary temperature of 20°C led to complete separation of As(V) and phosphate peaks. Results of these investigations together with recovery test data suggest that separation of the As species from soil solutions can be achieved in less than 5 min with detection limits of 0.50, 0.10, and 0.10 mg L⁻¹ for As(III), As(V), and DMA, respectively.

IT IS WELL ESTABLISHED that the toxicity of arsenic (As) is dependent on its chemical form. Arsenic is known to exist in natural soil and water environments in different oxidation states depending on the redox potential. Arsenite, As(III), is the most toxic of the common water-soluble species in environmental samples. The pentavalent species, As(V), is also relatively toxic, whereas the organoarsenic compounds such as the monomethyl arsinic acid (MMA) and DMA are much less toxic (Hodgson et al., 1988, p. 40–41). Speciation of As in natural samples is important in assessing exposure to toxic As compounds. Therefore, analytical methods that determine only the total amount of As present in samples do not adequately assess the danger of exposure. Moreover, a knowledge of the concentrations of As species is important in understanding the transport and biochemical processes involving As species in aquatic and soil water environments. Analytical data on As species, which have been difficult to quantify in natural soil and water samples, are not commonly found.

A number of instrumental techniques have been used to speciate As in the environment including ion chromatography (IC), high performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-

ICP-MS) (Thompson and Houk, 1986; Beauchemin et al., 1988), and IC coupled with ICP-MS (Sheppard et al., 1992). Speciation of As can also be achieved by supercritical fluid chromatography by complexing As(III) with bis(trifluoroethyl) dithiocarbamate (Laintz et al., 1992a,b). However, most of these methods are either difficult to perform, subject to interferences, or require expensive equipment.

Capillary zone electrophoresis (CZE) is a highly versatile analytical technique that is increasingly being used to speciate a wide variety of inorganic and organic species (Heckenberg et al., 1989; Jackson and Haddad, 1993; Jones and Jandik, 1991, 1992; Naidu, 1996; Naidu et al., 1998). This emerging technique allows for the rapid separation of charged compounds on the basis of differences in their electrophoretic mobilities. The more established technique of IC uses large volumes of mobile phase and requires a reasonably large sample size by comparison; on the other hand, CZE uses low volumes of electrolyte, typically achieves separations in <5 to 10 min, requires only nanoliters of sample, and the running costs are low. A number of investigators have previously reported the separation of As(III) and As(V) in standard solutions and spiked samples using CZE (e.g., Wildman et al., 1991; Morin et al., 1992). However, there are no reports in the literature on the speciation of As in soil water samples from contaminated sites. Most of the work reported in the literature (e.g., Morin et al., 1992) considers high concentrations of As that do not typify soil solution concentrations in contaminated soils. Information on the nature of As in soil solution and soil water extracts is important given that its toxicity to soil biota may vary with the nature of the species. Moreover, the mobility of As in soils may also vary with the nature of As species given that their partitioning to soil is dependent on their oxidation status. In this paper, we report the development of a new CZE method for the speciation of As in natural soil solution samples from contaminated sites in Australia.

MATERIALS AND METHODS

Instrumentation

A Waters Corporation (Milford, MA) model Quanta 4000 capillary ion analyzer equipped with a reversible-polarity power supply was used for the speciation and determination of As compounds. A fused silica capillary (72-cm by 50- μm i.d.) was used to separate the As species. The detection window was located approximately 64 cm from the injection point of

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Abbreviations: CZE, capillary zone electrophoresis; DMA, dimethylarsinic acid; HPLC, high performance liquid chromatography; IC, ion chromatography; ICP, inductively coupled plasma; MMA, monomethyl arsinic acid; MS, mass spectrometry; RCF, relative centrifugal force.

the capillary. Between each analysis, the capillary was flushed with buffer solution for 2 min. Ultraviolet detection (indirect) was carried out at 254 nm. The electropherograms were recorded and processed with Waters Millennium Chromatography Management Software. The capillary temperature and run voltage were varied between 20 to 35°C and 20 to 30 kV, respectively.

Sample Introduction

While a number of different modes of sample introduction are possible when using CZE, all injections in the present study were performed using hydrostatic injection. This involved (automatically) immersing the capillary in the sample, which is then raised to a height 10 cm above the running electrolyte level for 30 s. Following this operation, the sample chamber lowers back to the original level, after which the capillary is removed from the sample. The loaded capillary is then immersed into the running electrolyte and the voltage applied. Prior to sample introduction, a 2 min capillary purge is performed to remove any late migrating peaks remaining from the previous sample, i.e., the water peak. This is accomplished by a vacuum >0.08 MPa applied to the receiving electrolyte vial.

Soil Solutions

Surface and subsurface field moist soil samples from cattle tick dip As contaminated sites from northern New South Wales, Australia, were used to isolate soil solution for the analysis of soluble As. Duplicate samples (at field moisture capacity) were centrifuged at 3000 rpm (RCF 1075) for 2 h with a double jacket type centrifuge tube with an insert to collect soil solution. Soil solution (usually 2–5 mL/200g) collected at the base of the tube in the collection vessel was decanted into another centrifuge tube and centrifuged at 15 000 rpm (RC 26 890) for 90 min. Following the high speed centrifugation, soil solution was passed through a Millipore 0.2- μ m nylon filter. Subsamples were used for pH, electrical conductivity, speciation of As, and total chemical composition analyses. Arsenic in the soil solution was determined with hydride generation (Voth-Beach and Shrader, 1985).

Chemicals and Reagents

Standard Solutions

Commercially available sodium arsenite (NaAsO_2 of 99% purity), sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ of 99% purity), and dimethylarsinic acid (DMA of 98% purity) were used without further purification. NaAsO_2 was the chemical used during the tick eradication process. Following dissolution in water and with aging (or time) arsenious acid that is formed during the solution process oxidizes to arsenic acid. For this reason, fresh solutions were prepared daily during the speciation study using capillary electrophoresis.

Because MMA of analytical grade purity was not available, a reagent grade solution was used with CZE to identify the potential for separation of the As species. However, quantitation of MMA was not attempted in this study.

Stock solutions of arsenic species (100 mg L^{-1}) were prepared in Millipore (Bedford, MA) Milli-Q water and kept at -4°C as a precaution against any degradation. Calibration solutions ranging in concentration from blank to 10 mg L^{-1} were prepared from the stock solution as required. Since natural soil water samples contain a range of anions including Cl , SO_4 , NO_3 , and H_2PO_4 , the effects of these ions on As speciation were also investigated.

Electrolyte Buffer Solution

Chromate-based electrolytes have been demonstrated to give good performance in CZE, in terms of detection sensitivity and peak efficiency for high mobility anions (Heckenberg et al, 1989). The chromate-based electrolyte used in this work was prepared from a chromate concentrate containing $100 \text{ mmol L}^{-1} \text{Na}_2\text{CrO}_4$ (Mallinckrodt AR grade, Mallinckrodt, Inc., Chesterfield, MO) and $0.69 \text{ mmol L}^{-1} \text{H}_2\text{SO}_4$. Dilute acid is included to preadjust the electrolyte pH to ~ 8.0 when preparing the electrolyte buffer solution of 5 mmol L^{-1} chromate, in addition to 0.5 mmol L^{-1} of a proprietary Waters electroosmotic flow (EOF) modifier (CIA-Pak OFM Anion-BT). The pH of the resulting solution was 7.65. Milli-Q water was used for all dilutions and apparatus rinsing. A $100 \text{ mmol L}^{-1} \text{LiOH}$ solution was used for pH adjustment.

RESULTS AND DISCUSSION

Composition of Soil Solution

The composition of soil solution varied considerably among the soils examined. For instance, pH of the soil solutions ranged from 4.5 to 6.5 (with one exception that had a pH > 12) while dissolved organic carbon (as reflected by absorbance at 290 nm) was not detected in the soil solution. Typically, the concentrations of major cations and anions in the soil solution were generally high (Table 1). This was not surprising given that lime and phosphate were added during the pesticide stabilization process. The high concentration of Na ion is attributed to the nature of As pesticide used during the tick eradication process. Trace elements including Zn, Cu, and Mn were low in the soils and therefore these data are not presented here.

Selection of Operating Conditions

Effect of Electrolyte pH

The electrophoretic buffer solution pH had a significant effect on the separation of As species in standard solutions. When the instrument was run under the normal operating conditions (Heckenberg et al., 1989) for high mobility anions (20 kV run voltage, buffer pH of 8.13 and 20°C), separation was achieved for all three As species under study. However, the detection sensitivity for As(III) was poor (3 mg L^{-1}) compared with As(V) and DMA. Increasing buffer pH decreased migration times for all species. However, changes in migration time for As(V) (2.0 – 1.90 min) and DMA (2.8 – 2.65 min) were not as pronounced as was observed for As(III) (4.80 – 2.70 min).

Because As species under study are polyprotic acids,

Table 1. Descriptive statistics for soil solution composition of soils ($n = 22$) used in the present study.

| Measurement | Mean | SD | Min | Max | CV |
|-------------|--------------------|------|------|------|------|
| | mg L^{-1} | | | | % |
| Ca | 7.4 | 5.8 | 0.6 | 24.7 | 10.4 |
| K | 4.2 | 5.4 | 0.3 | 20.0 | 15.3 |
| Mg | 1.8 | 1.6 | 0.1 | 5.3 | 6.7 |
| Na | 3.5 | 2.1 | 1.1 | 8.8 | 6.8 |
| P | 3.5 | 2.3 | 0.0 | 7.5 | 12.4 |
| S | 4.1 | 2.6 | 0.4 | 9.8 | 5.8 |
| pH | 5.78 | 0.42 | 4.48 | 6.99 | 1.2 |

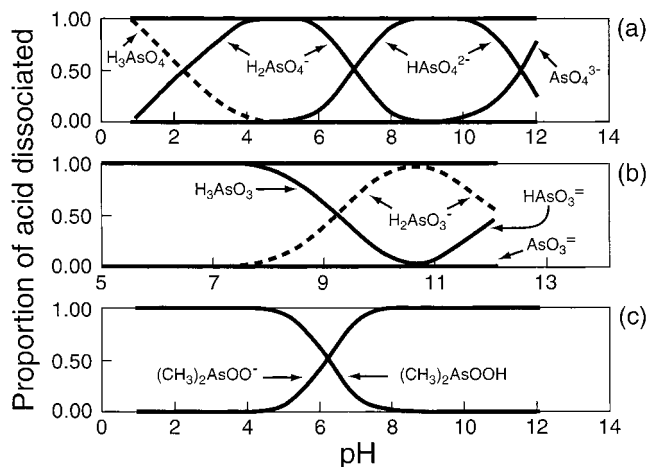


Fig. 1. Effect of solution pH on the proportion of acid dissociated based on the acid pK_a values.

their apparent charge is dependent on both their pK_a and carrier electrolyte pH values. Changes in ionic charge with changing pH will influence the mobility of the analyte species. Increasing pH will enhance the ionization of arsenic, arsenous, and dimethylarsinic acids. However, the extent of ionization varies considerably among the acids considered in the present study (Fig. 1). The deprotonation of acids leads to the formation of ions that vary considerably in their charge and in their ionic size to charge ratio. Such differences lead to vastly different mobilities. The analyte mobility in CZE is described by:

$$\mu = \mu_m + \mu_o,$$

where μ = mobility of the analyte in cm s^{-1} , μ_m = electrophoretic mobility, and μ_o = electroosmotic mobility.

Analyte mobility is the most important parameter determining separation efficiency and selectivity. Factors such as pH, ionic strength, potential drop across the capillary, and the temperature can be manipulated to improve separations through changes in analyte mobility. Because the composition of electrolyte, temperature, and the potential drop across the capillary is constant during a CZE separation, it is likely that the marked differences in the migration time is related to the dissociation of the protonated As species. The DMA is fully dissociated at pH 8 (Fig. 1). This explains the

observed constant migration time. Similar to DMA, 97% of arsenic acid is present in ionic form although the nature and proportion of the conjugate acid-base pair ($\text{H}_3\text{AsO}_4/\text{H}_2\text{AsO}_4^-$ and $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ etc) varies with increasing pH. For instance at pH 5, all the neutral molecule is dissociated into the diprotic form while at pH 10, 97% is present as HAsO_4^{2-} and only 3% as AsO_4^{3-} (Fig. 1). Therefore for these acids we expect a constant migration time. In contrast to As(V) and DMA, the migration time for As(III) is much longer at pH 8 because arsenious acid is largely present as uncharged species (94%) at pH 8 (Fig. 1).

Effect of Run Voltage and Capillary Temperature

When As(III) was detected using the normal operating conditions for high mobility anions (Waters CE manual), the detection, sensitivity and reproducibility were poor compared with As(V) and DMA. Changes in capillary temperature and run voltage affect several physical parameters such as viscosity, dielectric constant, dissociation constant of the ionizable species, and pH; these in turn affect the electroosmotic flow and the electrophoretic mobility of the analyte species. Both the run voltage and the capillary temperature were varied to investigate changes in the migration of As species. The results (Fig. 2) show that increasing the run voltage (a) and the temperature (b) reduced the anion migration time compared with those achieved under normal operating conditions with little loss in resolution. Observations over a range of temperatures and run voltages showed that operating conditions of 20 kV, 20°C, and a buffer pH of 11 gave the best overall separation for the standard As solution. However, the electropherogram obtained using these conditions consistently produced high background noise, making the detection of As(III) difficult at concentrations below 3 mg L^{-1} . Further studies varying pH, run voltage, and temperature revealed that a buffer pH of 8.13 and operating conditions of 25 kV, 30°C were the most effective conditions for determination of the As species. The electropherograms obtained for As(III), As(V), and DMA at different pH values ($[\text{As}] = 4 \text{ mg L}^{-1}$) using operating conditions of 25 kV, 30°C are presented in Fig. 3. These conditions were then applied to the speciation of As in soil water samples.

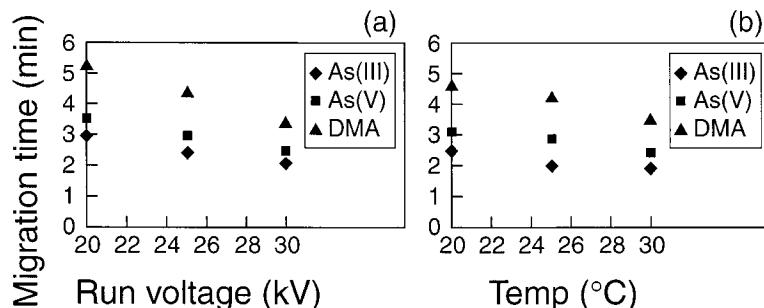


Fig. 2. Effect of runvoltage (a) and column temperature (b) on migration time of arsenic compounds. Separation column, 720-mm by 50- μm i.d. fused capillary tube; support electrolyte chromate buffer 5 mmol L^{-1} with 0.5 mmol L^{-1} EOF modifier; [pH 8.13 and $[\text{As}] = 2 \text{ mg L}^{-1}$].

Presence of Other Inorganic Anions

Initial attempts to determine As(V) in soil solution, proved to be very difficult because of interferences from other anions in the soil solution. Samples of standard solutions consisting of a mixture of inorganic anions (Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-}) ranging in concentrations from 0 to 10 mg L^{-1} were injected at optimum conditions as described above. Chloride, SO_4^{2-} , and NO_3^- did not interfere with the As peaks, orthophosphate comigrated with the As(V) species. Further studies using standard solutions revealed that orthophosphate solutions exceeding 0.1 mg L^{-1} caused an unacceptable positive interference for the As(V) species. This posed problems for the analysis of As in soil water extracts, given that the concentration of phosphate in soil solutions often exceed 0.10 mg L^{-1} .

Morin et al. (1992) found that at neutral or alkaline pH values for phosphate buffer solutions, the electrophoretic mobility of As species increased depending on the dissociation constant of the species. Examination of the pK_a values of the phosphoric ($\text{pK}_{a1} = 2.13$; $\text{pK}_{a2} = 7.20$; $\text{pK}_{a3} = 12.36$) and arsenic acid ($\text{pK}_{a1} = 2.19$, $\text{pK}_{a2} = 6.94$, $\text{pK}_{a3} = 11.50$) and the pH-dissociation curves (not presented here) suggests that differences in the extent of dissociation of the two acids is greatest above pH 10, possibly leading to variations in the migration times for these two anions. This is also consistent with the data in Fig. 4, which shows little difference in the mobilities of orthophosphate and As(V) at pH values 8.3, 9.2, and 10.0. When the carrier electrolyte pH exceeds 10, orthophosphate migrates more rapidly than As(V). This is not surprising given that the largest difference in the dissociation of these acids is associated with its third dissociation constant.

Separation efficiency is a measure of the analyte zone broadening which occurs during the chromatographic (or electrophoretic) process. Plate theory models a separation as a series of discrete sections termed "theoretical plates". The higher the theoretical plate number, the more efficient is the separation and the sharper are the resulting peaks (Robards et al., 1994, p. 49). In CZE, the use of narrow diameter capillaries leads to a flat electroosmotic flow profile, which results in high separation efficiencies compared with pressure driven techniques, such as HPLC, which have a parabolic flow profile (Naidu et al., 1998). The separation efficiency in CZE, in terms of the number of theoretical plates (N), is given by:

$$N = \mu V / 2D$$

where μ = analyte total mobility $\text{cm}^2 \text{ V s}^{-1}$; V = applied voltage, in volts; and D = solute diffusion coefficient, in $\text{cm}^2 \text{ s}^{-1}$.

This suggests that the number of theoretical plates is directly proportional to the applied voltage. Investigation into the effect of buffer pH at varying run voltages and temperatures showed that As(V) and orthophosphate ions comigrate at a run voltage of 20 kV at 20°C with a buffer pH of 8.13 (Fig. 5a). However, with increasing pH, these two species gradually separate so that at pH 10.01, they are well resolved. On the basis of these

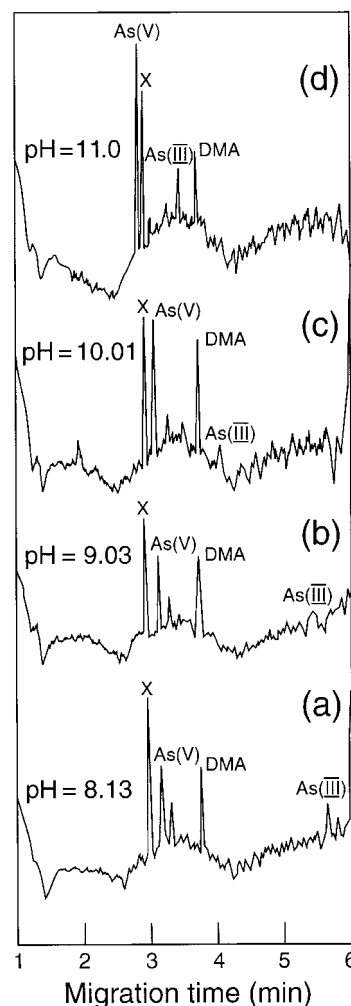


Fig. 3. Electropherograms of As species at different pH values using the operating conditions of 25 kV, 30°C (vertical axis in mV). Separation column, 720-mm by 50- μm i.d. fused capillary tube; support electrolyte chromate buffer 5 mmol L^{-1} with 0.5 mmol L^{-1} EOF; [As] = 2 mg L^{-1} . Peak "x" was not identified during the analysis.

results, As(V) determination in soil solution can be best carried out using a pH 10 chromate buffer with a run voltage of 20 kV and a capillary temperature of 20°C , while both DMA and As(III) are best analyzed using

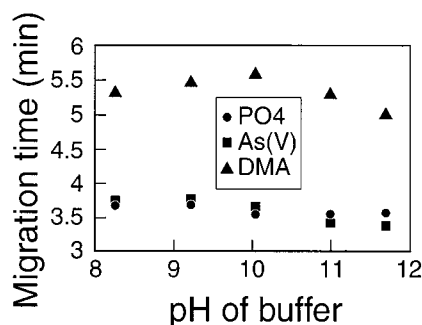


Fig. 4. Effect of pH of buffer solution on mean migration time of As(V), DMA and PO_4^{3-} with the vertical axis in mV. Separation column, 720-mm by 50- μm i.d. fused capillary tube; support electrolyte chromate buffer 5 mmol L^{-1} with 0.5 mmol L^{-1} EOF modifier; applied voltage 20 kV ([As] and [P] = 2 mg L^{-1}).

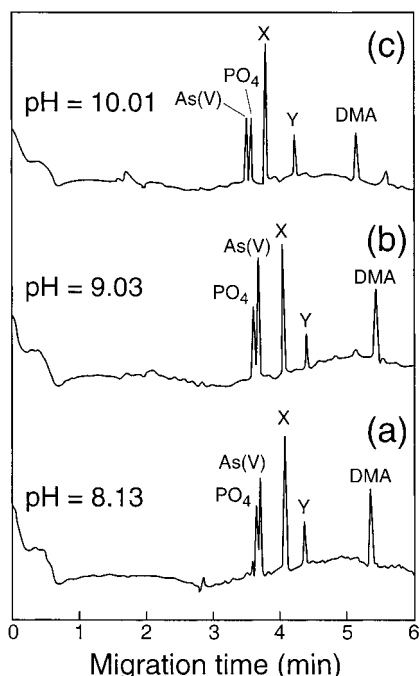


Fig. 5. Typical electropherograms of a soil solution at buffer pH values of 8.13 (a), 9.03 (b), and 10.01 (c). Separation column, 720-mm by 50- μ m i.d. fused capillary tube; support electrolyte chromate buffer 5 mmol L⁻¹ with 0.5 mmol L⁻¹ EOF modifier; applied voltage 20 kV, and 20°C. Peaks "x" and "y" were not identified during the analysis.

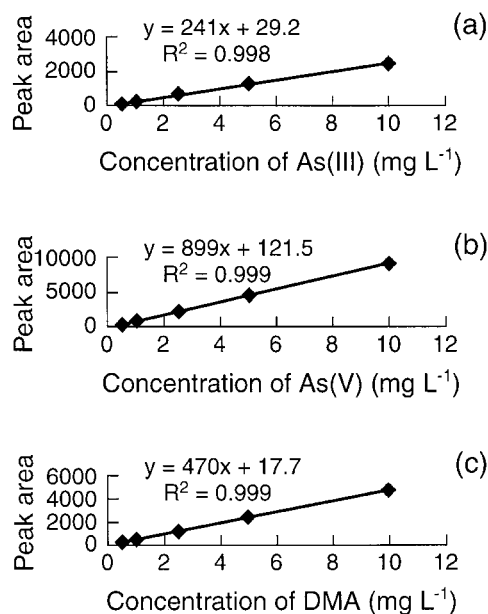


Fig. 6. Relationship between the concentration of As species and peak area. Separation column, 720-mm by 50- μ m i.d. fused capillary tube; support electrolyte chromate buffer 5 mmol L⁻¹ with 0.5 mmol L⁻¹ EOF modifier; applied voltage 25 kV and 30°C for As(III) and DMA and 20 kV and 20°C for As(V). pH of electrolyte for the separation of As(III) and DMA = 8.0; pH of electrolyte separation of As(V) = 10.0.

Table 2. Mean percentage recovery of As species added to soil solution samples using the instrumental conditions developed.

| Nature of species | Amount added | Recovery |
|-------------------|--------------------|----------|
| | mg L ⁻¹ | % |
| As(III) | 2 | 85 |
| | 5 | 92 |
| As(V) | 2 | 100 |
| | 5 | 117 |
| DMA† | 2 | 94 |
| | 5 | 96 |

† DMA, dimethylarsinic acid.

a pH 8 chromate-based buffer, a capillary temperature of 25°C and a run voltage of 30 kV.

Calibration Curves

Under the preferred conditions described above, plots of peak area and peak height against concentration were generated for the three As species (Fig. 6). The calibration curves based on peak area are linear with R^2 values >0.99 , whereas the calibration curves obtained using peak heights are non linear at As concentrations above 1 mg L⁻¹.

Detection Limits

The limit of detection of an analytical technique is generally evaluated from a knowledge of the standard deviation as a function of measurement level. A measured value is considered real when it is larger than the uncertainty associated with it. The point at which this occurs is defined arbitrarily as $3s_0$, where s_0 is the standard deviation of eight replicate measurements of the

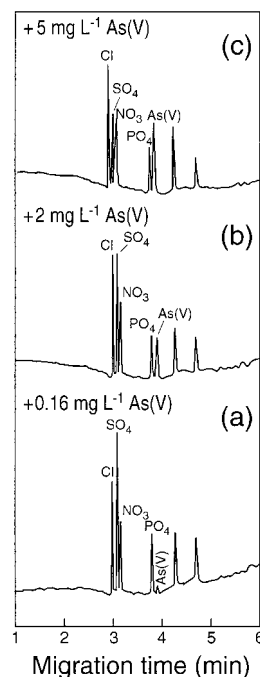


Fig. 7. Typical electropherograms of selected soil solutions following spiking of As(V) at 0.16, 2, and 5 mg L⁻¹. Capillary conditions were identical to those developed above. Separation column, 720-mm by 50- μ m i.d. fused capillary tube; support electrolyte chromate buffer 5 mmol L⁻¹ with 0.5 mmol L⁻¹ EOF modifier; applied voltage 20 kV and 20°C. pH of electrolyte separation of As(V) = 10.0.

buffer solution. On the basis of this procedure, the limits of detection for As(V), DMA, and As(III) were calculated to be 0.10, 0.10, and 0.5 mg L⁻¹, respectively.

Recovery Tests

Recovery tests were conducted with soil solutions ([As(V)] = 0.16 mg L⁻¹) that were spiked with varying concentrations of As(V), As(III), or DMA (Table 2). These studies revealed excellent agreement between the amounts of As(V), As(III), and DMA added to and recovered from soil solutions. An electropherogram typifying recovery data for As(V) is presented in Fig. 7. Between 85 and 117% of the added As species were recovered from the soil extracts with the highest recovery being for As(V) and the lowest for As(III). Similar recoveries were recorded with other soil solutions that were spiked with As(V).

Natural Soil Water Samples

Under the conditions developed above, As speciation was carried out in 25 soil solutions extracted from highly contaminated field moist soils. Typical electropherograms (Fig. 7) show peaks for As and other anions commonly found in soil solutions. However, apart from As(V), neither As(III) nor organoarsenic species were detected in the solutions isolated from field moist soils. With the exception of one soil solution, the concentration of As(V) was <2 mg L⁻¹. The exception was a highly alkaline soil (pH > 12) in which soil solution As was ~600 mg L⁻¹. The total As content of the sample with soil solution As exceeding 600 mg L⁻¹ was approximately 14 000 mg kg⁻¹ at a soil solution pH of 12.5. Given that there is limited information in the literature on the maximum permissible soil solution concentrations of As(V), it is difficult to draw meaningful conclusions concerning the potential threat to soil biota, but potential for As leaching exists. Absence of As(III) and organoarsenic species in the soil solutions is not surprising since the presence of both is dependent on Eh/pH conditions of the soil environment. Korte and Fernando (1991) report that arsenious species are stable under mildly reducing conditions and that the transition from As(V) to As(III) occurs at an Eh of -115 mV in soils with near neutral pH. Although the pH values of some of the soils under study were close to neutral, all the soils were well aerated, which is not conducive to formation of organoarsenic species.

Comparison with Hydride Generation

Korte and Fernando (1991) report that the ideal method for the quantitative determination of As in solutions is the hydride generation atomic absorption spectrophotometric technique because it is simple, rapid, convenient, and has the necessary sensitivity for the determination of ultra low levels (μg L⁻¹) of As. With this technique, As is converted to its hydride form followed by assay using atomic absorption spectrophotometry. Comparison of AAS generated data with CZE resulted in a 1:1 linear relationship with the As(V) data

obtained using the CZE method ($R^2 = 0.989$, $P < 0.001$). Since the AAS method provides an indication of total As in soil solution irrespective of the nature of species, the observed close 1:1 relationship confirms that the predominant form of As in the soil solution studied is As(V) and also that CZE can be useful tool for the speciation of As.

CONCLUSIONS

Arsenic in natural samples is commonly estimated by either ICP-AES or hydride generation atomic absorption spectrophotometry. Neither of these methods provides a basis for direct speciation of As which may exist in natural systems as a variety of species. Alternatively, CZE appears to be an appropriate technique for the speciation of AsO₃³⁻, AsO₄³⁻, and DMA in soil solutions. The separation of these species was achieved by optimizing the pH of the chromate-based electrolyte, capillary temperature, and run voltage. The limits of detection for As(V), DMA, and As(III) were found to be 0.10, 0.10, and 0.5 mg L⁻¹, respectively, while recovery data indicate that between 85 to 117% of spiked As species were recovered from soil extracts samples.

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REFERENCES

- Beauchemin, D., M.E. Bednas, S.S. Berman, J.W. McLaren, K.W.M. Siu, and R.E. Sturgeon. 1988. Identification and quantitation of arsenic species in a dogfish muscle reference material for trace elements. *Anal. Chem.* 60:2209-2212.
- Heckenberg, A.L., P.G. Alden, B.J. Wildman, J. Krol, J.P. Romano, P.E. Jackson, P. Jandik, and W.R. Jones. 1989. Waters innovative methods for ion analysis. Millipore Corporation, Marlborough, MA.
- Hodgson, E., R.B. Mailman, and J.E. Chambers. 1988. Dictionary of toxicology. Macmillan, London.
- Jackson, P.E., and P.R. Haddad. 1993. Capillary electrophoresis of inorganic ions and low-molecular-mass ionic solutes. *Trends Anal. Chem.* 12:231-238.
- Jones, W.R., and P. Jandik. 1991. Controlled changes of selectivity in the separation of ions by capillary electrophoresis. *J. Chromatogr.* 546:445-458.
- Jones, W.R., and P. Jandik. 1992. Various approaches to analysis of difficult sample matrices of anions using capillary ion electrophoresis. *J. Chromatogr.* 608:385-393.
- Korte, N.E., and Q. Fernando. 1991. A review of arsenic (III) in groundwater. *Crit. Rev. Environ. Contr.* 21:1-39.
- Laintz, K.E., J.J. Yu, and C.M. Wai. 1992a. Separation of metal ions with sodium bis(trifluoroethyl) dithio-carbamate chelation and supercritical fluid chromatography. *Anal. Chem.* 64:311-315.
- Laintz, K.E., J.M. Sjieh, and C.M. Wai. 1992b. Simultaneous determination of arsenic and antimony species in environmental samples using bis (trifluoroethyl) dihydrocarbamate chelation and supercritical fluid chromatography. *J. Chromatogr. Sci.* 30:120-123.
- Morin, P., M.B. Amran, S. Favier, R. Heimburger, and M. Leroy. 1992. Separation of arsenic anions by capillary zone electrophoresis with UV detection. *Fresenius J. Anal. Chem.* 342:357-362.
- Naidu, R. 1996. Application of capillary electrophoretic analytical technique to anion speciation and analyses in natural systems. p. 197-198. *In* Proceedings of Australian and New Zealand National Soils Conference, Melbourne 1-4 July. Australian Society of Soil Science, Melbourne, Australia.

Naidu, R., S. Naidu, P. Jackson, R.G. McLaren, and M.E. Sumner. 1998. Application of capillary electrophoresis to anion speciation in soil water extracts: I. Theory and Principles. *Adv. Agron.* 65: 131–150.

Robards, K., P.R. Haddad, and P.E. Jackson. 1994. Principles and practice of modern chromatographic methods. Academic Press, London.

Sheppard, B.S., J.A. Carusa, D.T. Heitkemper, and K.A. Wolnik. 1992. Arsenic speciation by ion chromatography with inductively coupled plasma mass spectrometric detection. *Analyst* 117:971–975.

Thompson, J.J., and R.S. Houk. 1986. Inductively coupled plasma mass spectrometric detection for multielement flow injection analysis and elemental speciation by reverse phase liquid chromatography. *Anal. Chem.* 58:2541–2548.

Voth-Beach, L.M., and D.E. Shrader. 1985. Reduction of interferences in the determination of arsenic and selenium by hydride generation. *Spectroscopy* 1:60–65.

Wildman, W.J., P.E. Jackson, W.R. Jones, and P.G. Alden. 1991. Analysis of anion constituents of urine by inorganic capillary electrophoresis. *J. Chromatogr.* 546:459–466.

Modeling Arsenic(III) Adsorption and Heterogeneous Oxidation Kinetics in Soils

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ABSTRACT

Arsenite [As(III)] is a soluble and toxic species of arsenic that can be introduced into soil by geothermal waters, mining activities, irrigation practices, and disposal of industrial wastes. We determined the rates of As(III) adsorption, and subsequent oxidation to arsenate [As(V)] in aerobic soil–water suspensions using four California soils. The rate of As(III) adsorption on the soils was closely dependent on soil properties that reflect the reactivity of mineral surfaces including citrate–dithionite (CD) extractable metals, soil texture, specific surface area, and pH. Heterogeneous oxidation of As(III) to As(V) was observed in all soils studied. The recovery of As(V) from As(III)-treated soils was dependent on levels of oxalate-extractable Mn and soil texture. After derivation of rate equations to describe the changes in soluble and recoverable As(III) and As(V) in soil suspensions, soil property measurements were used to normalize the empirically derived rate constants for three soils. The fourth soil, which had substantially different soil properties from the other three soils, was used to independently test the derived soil property–normalized model. The soil property–normalized consecutive reaction model gave a satisfactory description of the trends seen in the experimental data for all four soils. Understanding the effects of soil properties on the kinetics of chemical reactions of As(III) and As(V) in soils will be essential to development of quantitative models for predicting the mobility of As in the field.

THE OXIDATION of trace metals and metalloid oxyanions by soils has an important role in determining their mobility and toxicity. Reduced species such as As(III), Se(IV), and Cr(III) can be oxidized in soils to produce As(V), Se(VI), and Cr(VI), respectively. In the case of Se and Cr, the oxidized Se(VI) and Cr(VI) species are less strongly adsorbed to soils than Se(IV) and Cr(III) and thus are more mobile and bioavailable. The oxidation of As(III) produces As(V), which is strongly adsorbed in soils and is less toxic than As(III) (Knowles and Benson, 1983). Despite the fact that the reactions of As(III) with soil have been studied, the rates and mechanisms of As(III) adsorption, as well as oxidation to As(V), are still not well understood. The As(III) species can also be present in groundwater (Korte and

Fernando, 1991), and therefore the stability of As(III) after coming in contact with aerobic soils is of interest in environmental management.

Previous work on the reactions of As(III) with soil has focused primarily on As(III) adsorption rather than As(III) oxidation (Manning and Goldberg, 1997a; McGeehan and Naylor, 1994; Elkhatib et al., 1984). Iron oxides have been shown to be the most important mineral component in determining a soil's overall capacity to adsorb As(III) and As(V) (Jacobs et al., 1970; Fordham and Norrish, 1974, 1979; Elkhatib et al., 1984; Livesey and Huang, 1981; Manning and Goldberg, 1997a). It has also been concluded, using x-ray absorption spectroscopy (XAS), that As(V) is specifically adsorbed on synthetic Fe(III) oxide mineral surfaces (Waychunas et al., 1993; Fendorf et al., 1997). Electrophoretic mobility work (Pierce and Moore, 1982) has shown that As(III) is also specifically adsorbed on the Fe(III) oxide surface, and this has now been confirmed using Fourier transform infrared spectroscopy (Sun and Doner, 1996) and XAS (Manning et al., 1998).

The oxidation of As(III) to As(V) in soils has not been extensively studied despite the fact that this is an important reaction in the cycling of As in the environment. The oxidation of As(III) by lake sediments has been investigated (Oscarson et al., 1980, 1981) and it was concluded that an abiotic process involving Mn oxide minerals was directly responsible for As(III) oxidation. Heterogeneous oxidation of As(III) by synthetic Mn oxides (Oscarson et al., 1983; Scott and Morgan, 1995; Sun and Doner, 1998), and clay minerals (Manning and Goldberg, 1997b) has been shown, though very little is known about the rates or mechanisms of As(III) oxidation in whole soils. An improved understanding of the rate of As(III) oxidation in whole soil is necessary for the application of predictive models to describe As transport in the field. In addition, linking measurements of important soil properties with a quantitative description of the rate of As(III) adsorption and oxidation would improve the predictive capability of reactive transport models.

Given the need for a better understanding of the

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Abbreviations: CD, citrate–dithionite; DI, deionized; HPLC–HGAAS, high performance liquid chromatography–hydride generation atomic absorption spectrometry; Me_T, total citrate–dithionite extractable metals (Al + Fe + Mn); Mn_{OX}, oxalate-extractable manganese; SA, specific surface area; XAS, x-ray absorption spectroscopy; XRD, x-ray diffraction.